Characterization of Zirconium Sulfate Supported on Zirconia and Activity for Acid Catalysis

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Zirconium sulfate supported on zirconia catalysts were prepared by impregnation of powdered Zr(OH)₄ with zirconium sulfate aqueous solution followed by calcining in air at high temperature. The characterization of prepared catalysts was performed using Fourier transform infrared (FTIR), X-ray diffraction (XRD), differential scanning calorimetry (DSC), and by the measurement of surface area. The addition of zirconium sulfate to zirconia increased the phase transition temperature of ZrO₂ from amorphous to tetragonal due to the interaction between zirconium sulfate and zirconia, and the specific surface area and acidity of catalysts increased in proportion to the zirconium sulfate content up to 10 wt % of Zr(SO₄)₂·4H₂O. Infrared spectra of ammonia adsorbed on Zr(SO₄)₂/ZrO₂ showed the presence of Brønsted and Lewis acid sites on the surface. 10-Zr(SO₄)₂/ZrO₂ calcined at 600 °C exhibited maximum catalytic activities for 2-propanol dehydration and cumene dealkylation. The catalytic activities for both reactions were correlated with the acidity of catalysts measured by ammonia chemisorption method.

Keywords: Zirconium sulfate, Acid catalysis, 2-Propanol dehydration, Cumene dealkylation.

Introduction

It is known that the activity of a catalyst is greatly influenced by the method of catalyst preparation and the conditions of pretreatment. This is illustrated by the fact that the physical or chemical structure of a catalyst varies with the method of preparation, and that chemical species adsorbed on the surface affect the catalytic activity profoundly. The strong acidity of zirconia-supported sulfate has attracted much attention because of its ability to catalyze many reactions such as cracking, alkylation, and isomerization. The potential for a heterogeneous catalyst has yielded many papers on the catalytic activity of sulfated zirconia materials. Sulfated zirconia incorporating Fe and Mn has been shown to be highly active for butene isomerization, catalyzing the reaction even at room temperature.

It has been reported by several workers that the addition of platinum to zirconia modified by sulfate ions enhances catalytic activity in the skeletal isomerization of alkanes without deactivation when the reaction is carried out in the presence of hydrogen. The high catalytic activity and small deactivation can be explained by both the elimination of the coke by hydrogenation and hydroxylation, and the formation of Brønsted acid sites from H₂ on the catalysts. Recently, Hino and Arata reported zirconia-supported tungsten oxide as an alternative material in reaction requiring strong acid sites. Several advantages of tungstate, over sulfate, as an alternative material in reaction requiring strong acid sites. The acidic property of metal sulfate often gives high selectivity for diversified reactions such as hydration, polymerization, alkylation, cracking, and isomerization. However, structural and physicochemical properties of supported metal sulfates are considered to be in different states compared with bulk metal sulfates because of their interaction with supports.

Zirconium sulfate catalysts supported on zirconia have not been reported up to now.

This paper describes the characterization of zirconium sulfate supported on zirconia and its activity for acid catalysis. The characterization of the samples was performed by means of Fourier transform infrared (FTIR), X-ray diffraction (XRD), differential scanning calorimetry (DSC), and surface area measurements. For the acid catalysis, the 2-propanol dehydration and cumene dealkylation were used as test reactions.

Experimental Section

Catalyst preparation. The precipitate of Zr(OH)₄ was obtained by adding aqueous ammonia slowly into an aqueous solution of zirconium oxychloride (Junsei Chemical Co.) at room temperature with stirring until the pH of mother liquor reached about 8. The precipitate thus obtained was washed thoroughly with distilled water until chloride ion was not detected, and was dried at room temperature for 12 h. The dried precipitate was powdered below 100 mesh.

The catalysts containing various zirconium sulfate (Kanto Chemical Co.) contents were prepared by adding an aqueous solution of zirconium sulfate [Zr(SO₄)₂·4H₂O] to the Zr(OH)₄ powder followed by drying and calcining at high temperatures for 2 h in air. This series of catalysts are denoted by their weight percentage of Zr(SO₄)₂. For example,
5-Zr\((\text{SO}_4)_2\)/ZrO\(_2\) indicates the catalyst containing 5 wt % Zr\((\text{SO}_4)_2\).

Characterization. FTIR spectra were obtained in a heatable gas cell at room temperature using Mattson Model GL6030E FTIR spectrophotometer. The self-supporting catalyst wafers contained about 9 mg/cm\(^2\). Prior to obtaining the spectra the samples were heated under vacuum at 400-500 °C for 1.5 h. 

Catalysts were checked in order to determine the structure of the catalysts by means of a Philips X’pert-APD X-ray diffractometer, employing Cu K\(\alpha\) (Ni-filtered) radiation. 

DSC measurements were performed in air by a PL-STA model 1500H apparatus, and the heating rate was 5 °C per minute. For each experiment 10-15 mg of sample was used. 

The specific surface area was determined by applying the BET method to the adsorption of N\(_2\) at -196 °C. Chemisorption of ammonia was also employed as a measure of the acidity of catalysts. The amount of chemisorption was determined based on the irreversible adsorption of ammonia.\(^{20-22}\)

2-propanol dehydration was carried out at 160-180 °C in a pulse micro-reactor connected to a gas chromatograph. Fresh catalyst in the reactor made of 1/4 inch stainless steel was pretreated at 400 °C for 1 h in the nitrogen atmosphere. Diethylene glycol succinate on Shimazse was used as packing material of gas chromatograph and the column temperature was 150 °C for analyzing the product. Catalytic activity for 2-propanol dehydration was represented as mole of propylene converted from 2-propanol per gram of catalyst. Conversion for both reactions were taken as the average of the first to sixth pulse values.

Results and Discussion

Infrared spectra. The IR spectra of 10-Zr\((\text{SO}_4)_2\)/ZrO\(_2\) (KBr disc) calcined at different temperatures (400-800 °C) are given in Figure 1. 10-Zr\((\text{SO}_4)_2\)/ZrO\(_2\) calcined up to 700 °C showed IR absorption bands at 1205, 1112, 1063 and 1019 cm\(^{-1}\) which are assigned to bidentate sulfate ion coordinated to the metal such as Zr\(^{4+}\).\(^{22}\) However, for the calcination of 800 °C IR bands by the sulfate ion disappeared due to the complete decomposition of sulfate ion, as shown in Figure 1. These results are in good agreement with those of thermal analysis described later. 

In general, for the metal oxides modified with sulfate ion followed by evacuating above 400 °C, a strong band assigned to S=O stretching frequency is observed at 1380-1370 cm\(^{-1}\).\(^{23-25}\) In this work, the corresponding band for samples exposed to air was not found because water molecules in air were adsorbed on the surfaces of catalysts. These results are very similar to those reported by other authors.\(^{23-25}\) However, in a separate experiment IR spectrum of self-supported 10-Zr\((\text{SO}_4)_2\)/ZrO\(_2\) after evacuation at 400 °C for 2 h was examined, so that there was an intense band at 1376 cm\(^{-1}\) accompanied by broad and intense bands below 1250 cm\(^{-1}\) due to the overlapping of the ZrO\(_2\) skeletal vibration, indicating the presence of different adsorbed species depending on the treatment conditions of the sulfated sample.\(^{24}\)

Crystalline structures of catalysts. The crystalline structures of catalysts calcined in air at different temperatures for 2 h were examined. In the case of zirconia support, as shown in Figure 2, ZrO\(_2\) was amorphous to X-ray diffraction up to 300 °C, with a tetragonal phase at 350 °C, a two-phase mixture of the tetragonal and monoclinic forms at 700 °C, and a monoclinic phase at 900 °C. Three crystal structures of ZrO\(_2\), i.e., tetragonal, monoclinic, and cubic phases have been reported.\(^{26,27}\)

However, in the case of supported zirconium sulfate catalysts the crystalline structures of the samples were different from structure of the ZrO\(_2\) support. For the 5-Zr\((\text{SO}_4)_2\)/ZrO\(_2\), as shown in Figure 3, ZrO\(_2\) is amorphous up to 400 °C. In other words, the transition temperature from the amorphous to tetragonal phase was higher by 150 °C than that of pure ZrO\(_2\). X-ray diffraction data indicated a tetragonal phase of ZrO\(_2\) at 500-600 °C, a two-phase mixture of the tetragonal and monoclinic ZrO\(_2\) forms at 700 °C, and a monoclinic phase of ZrO\(_2\) at 800-900 °C. It is assumed that the interaction between zirconium sulfate and ZrO\(_2\) hinders the transition of
ZrO₂ from amorphous to tetragonal phase. These results are in good agreement with those of DSC described later. The presence of zirconium sulfate strongly influences the development of textural properties with temperature. For 5-Zr(SO₄)₂/ZrO₂, the crystalline phase of zirconium sulfate was not observed at any calcination temperature, indicating that most of zirconium sulfate is present as amorphous form and the zirconium sulfate is well dispersed on the surface of zirconia.

Moreover, for the sample of 15-Zr(SO₄)₂/ZrO₂ the transition temperature of ZrO₂ from amorphous to tetragonal phase was higher by 250 °C than that of pure ZrO₂. That is, the more the content of zirconium sulfate, the higher the phase transition temperature. However, as shown in Figure 4, X-ray diffraction patterns of 15-Zr(SO₄)₂/ZrO₂ were different from those of 5-Zr(SO₄)₂/ZrO₂. 15-Zr(SO₄)₂/ZrO₂ was amorphous to X-ray diffraction up to 500 °C, with a tetragonal phase of ZrO₂ at 600 °C and a two phase mixture of the tetragonal and monoclinic forms at 700-900 °C. However, as shown in Figure 4, the amount of monoclinic phase increased with the calcination temperature, indicating the easy phase transition from tetragonal to monoclinic form at high temperature.

It is also of interest to examine the influence of zirconium sulfate on the transition temperature of ZrO₂ from tetragonal to monoclinic phase. In view of X-ray diffraction patterns, the calcination temperature at which monoclinic phase is observed initially is 400 °C for pure ZrO₂ and 700 °C for 5-Zr(SO₄)₂/ZrO₂ and 15-Zr(SO₄)₂/ZrO₂, respectively. That is, the transition temperature increases with increasing zirconium sulfate content. This can also be explained in terms of the delay of transition from tetragonal to monoclinic phase due to the interaction between zirconium sulfate and zirconia, in analogy with the delay of transition from amorphous to tetragonal phase described above.
The XRD patterns of Zr(SO\(_4\))/ZrO\(_2\) containing different zirconium sulfate contents and calcined at 500 °C for 2 h are shown in Figure 5. ZrO\(_2\) is a tetragonal phase up to 10 wt %, but for samples containing high zirconium sulfate above 10 wt %, ZrO\(_2\) was amorphous because the interaction between zirconium sulfate and ZrO\(_2\) hinders the phase transition of ZrO\(_2\) from amorphous to tetragonal phase.

**Thermal analysis.** The X-ray diffraction patterns in Figures 3-5 clearly showed that the structure of Zr(SO\(_4\))/ZrO\(_2\) was different depending on the calcined temperature. To examine the thermal properties of precursors of Zr(SO\(_4\))/ZrO\(_2\) samples more clearly, their thermal analysis has been carried out as illustrated in Figure 6. For pure ZrO\(_2\), the DSC curve shows a broad endothermic peak below 180 °C due to water elimination, and a sharp and exothermic peak at 438 °C due to the ZrO\(_2\) crystallization. However, it is of interest to see the influence of zirconium sulfate on the crystallization of ZrO\(_2\) from amorphous to tetragonal phase. As Figure 6 shows, the exothermic peak due to the crystallization appears at 438 °C for pure ZrO\(_2\), while for Zr(SO\(_4\))/ZrO\(_2\) samples it is shifted to higher temperatures due to the interaction between Zr(SO\(_4\))\(_2\) and ZrO\(_2\). The shift increases with increasing zirconium sulfate content. Consequently, the exothermic peaks appear at 520 °C for 5-Zr(SO\(_4\))/ZrO\(_2\), 577 °C for 10-Zr(SO\(_4\))/ZrO\(_2\) and 618 °C for 15-Zr(SO\(_4\))/ZrO\(_2\). These results are in good agreement with those of X-ray results described above.

**Surface properties.** It is necessary to examine the effect of zirconium sulfate on the surface properties of catalysts, that is, specific surface area, acidity, and acid strength. The specific surface areas of samples calcined at 600 °C for 2 h are listed in Table 1. The presence of zirconium sulfate strongly influences the surface area in comparison with the pure ZrO\(_2\). Specific surface areas of Zr(SO\(_4\))/ZrO\(_2\) samples are much larger than that of pure ZrO\(_2\) calcined at the same temperature, showing that surface area increases gradually with increasing zirconium sulfate content up to 10 wt % of Zr(SO\(_4\)). It seems likely that the interaction between zirconium sulfate and ZrO\(_2\) protects catalysts from sintering.

The acidity of catalysts calcined at 600 °C, as determined by the amount of NH\(_3\) irreversibly adsorbed at 230 °C, is listed in Table 1. As listed in Table 1, the acidity increases abruptly upon the addition of zirconium sulfate [0.5 wt % of Zr(SO\(_4\))\(_2\)].

![Figure 5](image1.png)  
**Figure 5.** X-ray diffraction patterns of Zr(SO\(_4\))/ZrO\(_2\) having various Zr(SO\(_4\))\(_2\) contents and calcined at 500 °C for 2 h: ○, tetragonal phase of ZrO\(_2\); ●, monoclinic phase of ZrO\(_2\).

![Figure 6](image2.png)  
**Figure 6.** DSC curves of precursor for Zr(SO\(_4\))/ZrO\(_2\) having different Zr(SO\(_4\))\(_2\) contents; (a) ZrO\(_2\), (b) 5-Zr(SO\(_4\))/ZrO\(_2\), (c) 10-Zr(SO\(_4\))/ZrO\(_2\), (d) 15-Zr(SO\(_4\))/ZrO\(_2\), (e) 20-Zr(SO\(_4\))/ZrO\(_2\), (f) 25-Zr(SO\(_4\))/ZrO\(_2\), and (g) Zr(SO\(_4\))\(_2\)·4H\(_2\)O.

<table>
<thead>
<tr>
<th>Catalysts</th>
<th>Surface area (m(^2)/g)</th>
<th>Acidity (µmol/g)</th>
</tr>
</thead>
<tbody>
<tr>
<td>ZrO(_2)</td>
<td>56.1</td>
<td>41.3</td>
</tr>
<tr>
<td>0.5-Zr(SO(_4))(_2)/ZrO(_2)</td>
<td>99.2</td>
<td>104.9</td>
</tr>
<tr>
<td>1-Zr(SO(_4))(_2)/ZrO(_2)</td>
<td>109.4</td>
<td>108.6</td>
</tr>
<tr>
<td>3-Zr(SO(_4))(_2)/ZrO(_2)</td>
<td>126.9</td>
<td>145.7</td>
</tr>
<tr>
<td>5-Zr(SO(_4))(_2)/ZrO(_2)</td>
<td>137.9</td>
<td>160.3</td>
</tr>
<tr>
<td>10-Zr(SO(_4))(_2)/ZrO(_2)</td>
<td>142.3</td>
<td>168.1</td>
</tr>
<tr>
<td>15-Zr(SO(_4))(_2)/ZrO(_2)</td>
<td>124.3</td>
<td>137.2</td>
</tr>
<tr>
<td>20-Zr(SO(_4))(_2)/ZrO(_2)</td>
<td>110.4</td>
<td>126.8</td>
</tr>
<tr>
<td>25-Zr(SO(_4))(_2)/ZrO(_2)</td>
<td>66.2</td>
<td>78.7</td>
</tr>
</tbody>
</table>
Characterization of Zr(SO$_4$)$_2$/ZrO$_2$ and Acid Catalysis


Zr(SO$_4$)$_2$ to ZrO$_2$, and then the acidity increases very gently with increasing zirconium sulfate content up to 10 wt% of Zr(SO$_4$)$_2$. In view of Table 1, it is clear that the acidity runs parallel with the surface area. That is, the higher the surface area, the more the acidity.

Infrared spectroscopic studies of ammonia adsorbed on solid surfaces have made it possible to distinguish between Brønsted and Lewis acid sites. Figure 7 shows the IR spectra of ammonia adsorbed on 10-Zr(SO$_4$)$_2$/ZrO$_2$ samples evacuated at 400 °C for 1 h. For 10-Zr(SO$_4$)$_2$/ZrO$_2$ the band at 1443 cm$^{-1}$ is the characteristic peak of ammonium ion, which is formed on the Brønsted acid sites and the absorption peak at 1622 cm$^{-1}$ is contributed by ammonia coordinately bonded to Lewis acid sites, indicating the presence of both Brønsted and Lewis acid sites on the surface of 10-Zr(SO$_4$)$_2$/ZrO$_2$ sample. Other samples having different zirconium sulfate content also showed the presence of both Lewis and Brønsted acids. As Figure 7(a) shows, the intense band at 1376 cm$^{-1}$ after evacuation at 400 °C is assigned to the asymmetric stretching vibration of S=O bonds having a high double bond nature. However, the drastic shift of the IR band from 1376 cm$^{-1}$ to lower wavenumber (not shown due to the overlaps of skeletal vibration bands of ZrO$_2$) after ammonia adsorption [Figure 7(b)] indicates a strong interaction between an adsorbed ammonia molecule and the surface complex. Namely, the surface sulfur compound in the highly acidic catalysts has a strong tendency to reduce the bond order of SO from a highly covalent double-bond character to a lesser double-bond character when a basic ammonia molecule is adsorbed on the catalysts. Acid stronger than H$_2$O is superacids. The strong ability of the sulfur complex to accommodate electrons from a basic molecule such as ammonia is a driving force to generate superacidic properties. Consequently, Zr(SO$_4$)$_2$/ZrO$_2$ catalysts would be solid superacids, in analogy with the case of ZrO$_2$ modified with sulfate group.

Catalytic activities for acid catalysis. It is interesting to examine how the catalytic activity of acid catalyst depends

Figure 8. Catalytic activities of Zr(SO$_4$)$_2$/ZrO$_2$ for 2-propanol dehydration as a function of Zr(SO$_4$)$_2$ content.

Figure 9. Catalytic activities of Zr(SO$_4$)$_2$/ZrO$_2$ for cumene dealkylation as a function of Zr(SO$_4$)$_2$ content.
on the acid property. The catalytic activities for the 2-propanol dehydration are measured and the results are illustrated as a function of Zr(SO\textsubscript{4})\textsubscript{2} content in Figure 8, where reaction temperatures are 160-180 °C. In view of Table 1 and Figure 8, the variations in catalytic activity for 2-propanol dehydration are well correlated with the changes of their acidity, showing the highest activity and acidity for 10-Zr(SO\textsubscript{4})\textsubscript{2}/ZrO\textsubscript{2}. It has been known that 2-propanol dehydration takes place very readily on weak acid sites.\cite{32,33} Good correlations have been found in many cases between the acidity and the catalytic activities of solid acids. For example the rates of both the catalytic decomposition of cumene and the polymerization of propylene over SiO\textsubscript{2}-Al\textsubscript{2}O\textsubscript{3} catalysts were found to increase with increasing acid amounts at strength H\textsubscript{o} ≤ +3.3.\cite{34} It was also reported that the catalytic activity of nickel silicates in the ethylene dimerization as well as in the butene isomerization was closely correlated with the acidity of the catalyst.\cite{35}

Cumene dealkylation takes place on relatively strong acid sites of the catalysts.\cite{32,33} Catalytic activities for cumene dealkylation against Zr(SO\textsubscript{4})\textsubscript{2} content are presented in Figure 9, where reaction temperature is 350-400 °C. Comparing Table 1 and Figure 9, the catalytic activities are also correlated with the acidity. The correlation between catalytic activity and acidity holds for both reactions, 2-propanol dehydration and cumene dealkylation, although the acid strength required to catalyze acid reaction is different depending on the type of reactions. As seen in Figures 8 and 9, the catalytic activity for cumene dealkylation, in spite of higher reaction temperature, is lower than that for 2-propanol dehydration.

Catalytic activities of 10-Zr(SO\textsubscript{4})\textsubscript{2}/ZrO\textsubscript{2} are plotted as a function of calcination temperature for 2-propanol dehydration in Figure 10. The activities increased with the calcination temperature, giving a maximum at 600 °C and then the activities decreased. Catalytic activities of 10-Zr(SO\textsubscript{4})\textsubscript{2}/ZrO\textsubscript{2} for cumene dealkylation are also plotted as a function of calcination temperature in Figure 11. The activities also exhibited a maximum at 600 °C. The decrease of activity for both reactions above 600 °C can be probably attributed to the fact that the surface area and acidity above 600 °C decrease with the calcination temperature.

**Conclusions**

This paper has shown that a combination of FTIR, DSC, and XRD can be used to characterize Zr(SO\textsubscript{4})\textsubscript{2}/ZrO\textsubscript{2} prepared by impregnation of powdered Zr(OH)\textsubscript{4} with zirconium sulfate aqueous solution followed by calcining in air. The interaction between zirconium sulfate and zirconia influenced the physicochemical properties of prepared catalysts with calcination temperature. The presence of zirconium sulfate delays the phase transitions of ZrO\textsubscript{2} from amorphous to tetragonal and from tetragonal to monoclinic. The specific surface area and acidity of catalysts increase proportionally with the zirconium sulfate content up to 10 wt % of Zr(SO\textsubscript{4})\textsubscript{2} in catalysts. The proportional increment between catalytic acidity and acidity holds for both reactions, 2-propanol dehydration and cumene dealkylation, although the acid strength required to catalyze acid reaction is different depending on the type of reactions.

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